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The role of metals in methane production from shredder waste in landfills

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Shredder waste (SW) is the waste produced after mechanical treatment of iron and metal containing wastes including vehicles, bicycles, and white goods. SW consists of mainly plastic, metals, rubber, textile, foam, glass and wood. Relatively high production of methane (CH₄) has been observed at SW monofills (Mønster et al., 2015; Scheutz et al., 2011). This is surprising as SW usually contains low fractions of biodegradable waste and the biodegradable fractions have a high content of lignocellulosic components such as wood and cardboard. The reason for high CH₄ production from SW is unknown. Moreover, previous studies have shown gas compositions in SW, which differed from conventional landfill gas—a high CH₄ content and very low or no CO₂ (Olsen and Willumsen, 2013; Scheutz et al., 2011). The reason for the unusual gas composition is also unknown.

Although SW has passed through metal-separation technologies, it still contains metals. We hypothesized that high CH₄ production from SW and unusual gas composition could be due to H₂ production by biocorrosion of metals in the waste, supporting hydrogenotrophic methanogens to convert CO₂ to CH₄, resulting in higher CH₄ content and lower CO₂. The objective of this study was to investigate the role of metals contained in SW in CH₄ production from SW.

SW samples were collected from Odense Nord landfill located in Funen, Denmark. SW samples were taken by an excavator according to the year of deposition: 2009 and 2012. Fresh samples of SW (year 2015) were obtained by sampling the waste on the same day as it was deposited in the waste cell. Samples from 2009, 2012 and fresh sample were mixed together based on equal wet weight to make one composite sample (COM), representative of the whole landfill. Two sets of experiments were performed: biocorrosion experiment and batch incubation experiment.

Biocorrosion experiments were conducted to investigate hypothesis of CH₄ yield enhancement by H₂ production from biocorrosion of metals. According to the conducted literature review Fe, Al, Zn and Cu are the main metals in SW and thus were examined for their ability to produce H₂. The experiment had two steps and both were carried out in duplicate in 1 L glass bottles for 20 days in a 37 °C incubator. In the first step, H₂ production from elemental metals in contact with water was investigated. In this step, 2.5 g of elemental metals was placed in each incubation bottle and 250 mL of tap water was added to each. In step two, the CH₄ production enhancement of inoculum by addition of metals was investigated. In this step, incubation bottles contained 2.5 g of elemental metals and 250 g of inoculum, resulting a concentration of 10 g/L of liquid for each metal. Bottles containing only inoculum were used as blank to calculate CH₄ production from inoculum alone. Bottles were flushed with N₂ for 15 minutes to establish an anaerobic condition, and then sealed with rubber septum.

Batch incubation experiments were performed in glass bottles with total volumes of 5 L at 37 °C. In order to investigate the role of metals on the CH₄ production, Fe, Al, Zn, and Cu with dimension of 5 mm × 5 mm and concentrations of 5, 2, 2, and 2 % of the substrate wet weight (25, 10, 10, 10 g/L of liquid), respectively, were added separately to the incubation bottles containing the COM samples. Moisture content of the samples was adjusted to 75 % w/w, and inoculum (30 % of substrate wet weight) was added to the incubation bottles. One bottle containing only inoculum and water were used as blank to determine CH₄ production from the inoculum alone, which was subtracted from the CH₄ production of waste samples. Abiotic control experiments were also performed by sterilizing samples (autoclaving three times for 1 h at 121 °C) to measure possible CH₄ production due to non-microbial processes. All reactors were flushed for 20 minutes with nitrogen gas to make an anaerobic condition.

The first step of biocorrosion experiment showed that H₂ can be produced by Fe, Al, and Zn, but not by Cu. The second step of biocorrosion experiments results showed that adding Fe, Al and Zn to inoculum resulted in higher CH₄ generation than inoculum alone. However, addition of Cu to inoculum resulted in lower CH₄ production in comparison to inoculum alone.

Figure 1 shows cumulative CH₄ production curves of all waste samples during 148 days incubation time. As it can be seen from Figure 1 sterilized reactors did not produce CH₄, indicating there was no abiotic production of CH₄ from SW. Addition of Al and Zn to the COM samples resulted in higher CH₄ production compared to experiments with COM alone, while the addition of Fe and Cu resulted in lower CH₄ production. The obtained result for the impact of Al, Zn and Cu on CH₄ production is in line with the biocorrosion experiment. However, adding Fe resulted in lower CH₄ production in this experiment, while it resulted in higher CH₄ production in the biocorrosion experiment. This could be due to a higher concentration of Fe in this

experiment (25 g/L) compared to the biocorrosion experiment (10 g/L). When comparing the headspace CO₂ concentrations of COM reactor with COM+Al and COM+Zn reactors, it was observed that COM+Al and COM+Zn reactors have lower headspace CO₂ and higher CH₄ concentrations. This could be due to utilization of produced H₂ by corrosion of Al and Zn and existing CO₂ in produced biogas by methanogens, resulting in higher CH₄ and lower CO₂ in the headspace of these reactors.

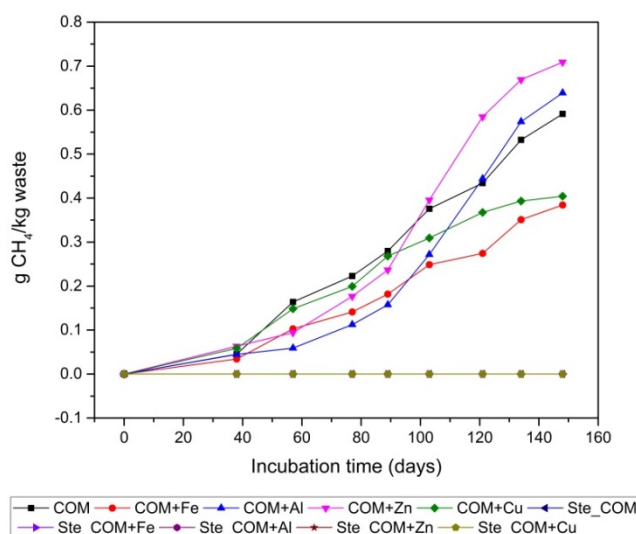


Figure 1. Cumulative CH₄ generation from SW, during period of 148 days. Please note that CH₄ production from sterilized reactors (starting with "Ste") were all zero and thus the curves are on top of each other and not visible on the graph.

In conclusion, it was evident from the incubation experiments that CH₄ production from SW was not abiotic. Al and Zn were found to produce H₂, and it was observed that the produced H₂ can be consumed by methanogens to convert CO₂ to CH₄. Moreover, results of the incubation experiments indicated that the unusual gas composition (higher CH₄ and lower CO₂), and the relatively high CH₄ production rate from landfilling of SW is most likely due to the consumption of existing CO₂ in the produced biogas and H₂ produced by biocorrosion of Al and Zn by methanogens.

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